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n- and *p*-type dopants for cubic silicon nitride

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The formation and ionization energies of impurities in cubic silicon nitride are investigated through first-principles calculations. Among the elements in the groups III to VI, P and O are preferable for *n*-type doping, while Al is favorable for *p*-type doping in terms of the formation and ionization energies. The compensation of doped carriers associated with the incorporation of these impurities into anti and interstitial sites can be suppressed if appropriate growth conditions are chosen. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1354667]

Silicon nitride (Si_3N_4) is important as a structural component. It is also used as an insulating layer in the silicon technology. Hexagonal Si_3N_4 crystals (α and β) as well as amorphous films have thus far been utilized for these applications. In 1999, a third crystalline phase of Si_3N_4, i.e., Si_3N_4 in the cubic spinel structure (c-Si_3N_4), was discovered.[1] A first-principles calculation within the local density approximation then suggested that c-Si_3N_4 has a direct band gap of 3.45 eV.[2] This is in contrast to wider and indirect band gaps of α- and β-Si_3N_4 estimated through similar calculations.[3] The direct band gap implies the potential applications of c-Si_3N_4 as optical or electronic devices in addition to the structural applications. In order to use c-Si_3N_4 as a semiconductor, it is essential to find good dopants. In the present letter, we report the results of first-principles calculations on various kinds of *n*- and *p*-type dopants for c-Si_3N_4; the information should be useful for the search of conducting Si_3N_4 that may rival the preexisting semiconductors.

The calculations were performed for 56-atom supercells containing impurities by a first-principles plane-wave pseudopotential method[4] within the generalized gradient approximation.[5] Ultrasoft pseudopotentials[6] were employed with a plane-wave cutoff energy of 360 eV, which was confirmed to achieve the convergence of the formation energies of the impurities within 0.05 eV for cutoff energies up to 700 eV. Numerical integration over the Brillouin zone was carried out at the Γ point. The positions of atoms within the second nearest neighbors of the impurities were relaxed under a constant volume condition, using the lattice constant optimized for the perfect crystal of c-Si_3N_4.[7] The relaxation procedures were truncated when all the residual forces for the relaxed atoms were less than 0.1 eV/Å.

As for impurity species, we consider B, Al, and Ga from the group III, and P and As from the group V to substitute for Si. C from the group IV, and O and S from the group VI are adopted to substitute for N. The other elements in these groups are not investigated since they are unlikely to be doped effectively due to the significant size mismatch. For the Si-site substitution, the two types of Si sites in the spinel structure, i.e., the tetrahedral and octahedral sites of the N sublattice in the face-centered cubic structure, are considered.

Using the total energies of the supercells, the formation and ionization energies of the impurities were calculated. The formation energy is given as a function of the atomic chemical potentials and the Fermi energy, i.e.,[8,9]

$$E_{\text{formation}}(q) = E_T(q) - n_{\text{Si}}\mu_{\text{Si}} - n_{\text{N}}\mu_{\text{N}} - \mu_i + qE_F, \qquad (1)$$

where E_T is the total energy of a supercell containing an impurity atom in a charge state q. n_{Si} and n_{N} are the number of Si and N atoms in the supercell. μ_{Si}, μ_{N} and μ_i are the chemical potentials of Si, N and impurity atoms. E_F is the Fermi energy or the electron chemical potential. μ_{Si} and μ_{N} are variables correlated as

$$3\mu_{\text{Si}} + 4\mu_{\text{N}} = \mu_{c\text{-}Si_3N_4(\text{bulk})}, \qquad (2)$$

where $\mu_{c\text{-}Si_3N_4(\text{bulk})}$, the chemical potential of the bulk c-Si_3N_4, is a constant value calculated as the total energy of c-Si_3N_4 per unit formula. The total energies per atom for the bulk Si and α-N_2 were chosen as the upper limits of μ_{Si} and μ_{N}, respectively. When μ_{Si} and μ_{N} violate these limits, the bulk c-Si_3N_4 is thermodynamically unstable. Likewise, μ_i should vary within the range that the impurity element does not segregate, i.e., the upper limit is determined by the solubility limit. Assuming values of μ_{Si}, μ_{N}, and μ_i in these ranges, we can discuss the formation energies of the impurities in c-Si_3N_4 under a growth condition.

The ionization energies were evaluated as the difference between the formation energies of the neutral and charged impurities when the Fermi energy is the same as the minimum of the conduction band[10] and the maximum of the valence band for positive ionization (*n*-type doping) and negative ionization (*p*-type doping), respectively.

The calculated ionization and formation energies are listed in Table I. The ionization energies are those of single ionization; further ionization was found to be much higher in energy and hence unlikely for all the impurities considered here. The formation energies are calculated for the neutral charge state at the solubility limits under the two extreme conditions, i.e., the Si-rich limit ($\mu_{\text{Si}} = \mu_{\text{Si(bulk)}}$ and μ_{N}

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TABLE I. Ionization and formation energies of impurities in c-Si_3N_4. The formation energies are calculated for the neutral charge state at the solubility limits that are determined by the equilibrium conditions with the simple substances or the compounds shown as segregants; the energies in the parentheses are determined by the simple substances, whereas the others are determined by the compounds.

Doping type	Impurity element	Substitution site	Ionization energy (eV)	Formation energy (eV)		
				Si-rich	N-rich	Segregants
n	P	Si(tet)	0.1	6.7	(0.3)	SiP
		Si(oct)	0.4	6.4	(0.0)	
	As	Si(tet)	0.0	5.8	(2.4)	SiAs
		Si(oct)	0.8	5.2	(1.8)	
	O	N	0.1	2.3	3.1	SiO_2 (α quartz)
	S	N	0.1	5.4	(6.7)	SiS_2
p	B	Si(tet)	−0.1	4.2	3.4	c-BN
		Si(oct)	0.0	5.7	4.9	
	Al	Si(tet)	0.0	2.6	1.8	w-AlN
		Si(oct)	0.1	2.5	1.7	
	Ga	Si(tet)	0.2	(3.7)	2.0	w-GaN
		Si(oct)	0.5	(4.6)	2.9	
	C	N	0.7	3.3	(5.0)	β-SiC

$=1/4\mu_{c\text{-}Si_3N_4(bulk)}-3/4\mu_{Si(bulk)}$) and the N-rich limit ($\mu_{Si}=1/3\mu_{c\text{-}Si_3N_4(bulk)}-4/3\mu_{N(bulk)}$ and $\mu_N=\mu_{N(bulk)}$). The solubility limits are assumed to be the conditions that either the simple substances or the compounds shown in Table I just start to segregate. In other words, c-Si_3N_4 doped with the impurities is in equilibrium with the simple substances or the compounds at the limits.[11] For the Si-site substitution, N-rich conditions are preferable in formation energy, whereas Si-rich conditions are preferable for the N-site substitution, as recognized for the Si- and N-rich limits in Table I. Note that the ionization energies and the differences between the formation energies for the Si(tet) and Si(oct) sites are independent of the atomic chemical potentials.

For the *n*-type doping, all the impurities exhibit the ionization energies of lower than 0.1 eV. Regarding the P and As impurities substituting for Si, only the doping into the tetrahedral sites should be effective since the ionization energies for the octahedral sites are too high. When the tetrahedral sites are occupied, the formation energies at the solubility limits under the extreme N-rich condition are 0.3 and 2.4 eV for the P and As impurities. The significant difference in formation energy should suggest that the P impurities are preferable to substitute for Si although the ionization energy is 0.1 eV higher than that of the As impurities.

Concerning the N-site substitution, the O and S impurities show approximately the same ionization energies. As for the formation energies, the S impurities are too high even at the Si-rich limit. This implies that the S impurities are hard to be doped. We therefore suggest that the O impurities are preferable to substitute for N.

Turning to the *p*-type doping, the B and Al impurities at the Si sites show the ionization energies of lower than 0.1 eV. In terms of the formation energies, however, the Al impurities are clearly preferable. The Al impurities are likely to be doped into both of the Si(tet) and Si(oct) sites in nearly the same magnitude of concentration since the formation energies for these sites are comparable. On the other hand, the Ga and C impurities exhibit high ionization and formation energies. These impurities cannot act as effective acceptors.

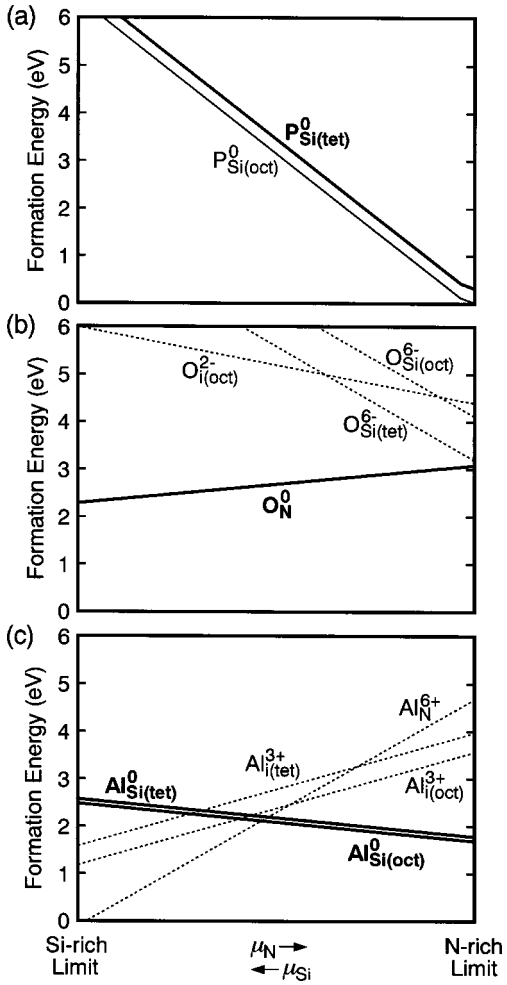

FIG. 1. Formation energies at the solubility limits as a function of the Si or N chemical potential for (a) P, (b) O, and (c) Al impurities. The Fermi energy is taken to be the minimum of the conduction band for P and O as *n*-type dopants, and to be the maximum of the valence band for Al as a *p*-type dopant. The superscripts indicate the charge states. The subscripts indicate the impurity sites; e.g., Si(tet) and i(oct) are the tetrahedral Si lattice site and the octahedral interstitial site of the N sublattice. For each site, the charge state that gives the lowest formation energy is shown. The formation energies of the impurities at the normal sites and the sites associated with compensation are shown with bold and dotted lines, respectively.

We therefore propose that the Al impurities are the best candidate for *p*-type dopants.

We now consider the incorporation of the P, O, and Al impurities into other sites; these candidates may compensate carrier electrons or holes when they occupy anti or interstitial sites. Therefore, the calculation for these sites should be important. Figure 1 shows the formation energies of the P, O, and Al impurities occupying the normal substitutional sites that we discussed above, the other substitutional (anti) sites, and the tetrahedral and octahedral interstitial sites of the N sublattice. The formation energies are calculated at the solubility limits, assuming the Fermi energy to be the minimum of the conduction band for P and O as *n*-type dopants, and to be the maximum of the valence band for Al as a *p*-type dopant. For each impurity site, the charge state that gives the lowest formation energy is shown. The positive and negative charge states at anti and interstitial sites indicate that the impurities occupying these sites can compensate carrier holes and electrons, respectively.

Concerning the normal substitutional sites, N-rich conditions are preferable in formation energy for the P and Al impurities, while Si-rich conditions are favorable for the O impurities as mentioned above. Under these conditions, the formation energies of the P, O, and Al impurities at the antistitial and interstitial sites are quite higher than those for the normal sites. This implies that the compensation of carriers should not be a serious problem. However, the formation energies are dependent on the atomic chemical potentials, as recognized in Fig. 1. When we choose the opposite conditions of the chemical potentials, the formation energies for the normal sites and the sites associated with compensation become comparable or overturned for the O and Al impurities. The choice of growth conditions is therefore very important for effective doping.

In summary, we have investigated the formation and ionization energies of the impurities in c-Si_3N_4 through first-principle calculations. The P and O impurities are suggested to be preferable for the *n*-type doping, while the Al impurities are favorable for the *p*-type doping. The compensation of doped carriers associated with the incorporation of these impurities into anti and interstitial sites can be suppressed if appropriate growth conditions are chosen. The present information on the dopants should be useful in the search of semiconducting c-Si_3N_4.

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[10] Calculated to be 3.6 eV above the maximum of the valence band. This energy was evaluated as $\{E^{(1)}-E^{(0)}\}-\{E^{(0)}-E^{(-1)}\}$, where $E^{(N)}$ indicates the total energy of the perfect lattice supercell with additional N electrons. The value agrees with a band gap in the one-electron band structure.
[11] Under the equilibrium conditions, the chemical potentials of the impurities were determined using the total energies of the simple substances and the compounds, which were calculated after the optimization of the structure.